Practical silicon deposition rules derived from silane monitoring during plasma-enhanced chemical vapor deposition

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We clarify the difference between the SiH4 consumption efficiency η and the SiH4 depletion fraction D, as measured in the pumping line and the actual reactor of an industrial plasma-enhanced chemical vapor deposition system. In the absence of significant polysilane and powder formation, η is proportional to the film growth rate. Above a certain powder formation threshold, any additional amount of SiH4 consumed translates into increased powder formation rather than into a faster growing Si film. In order to discuss a zero-dimensional analytical model and a two-dimensional numerical model, we measure η as a function of the radio frequency (RF) power density coupled into the plasma, the total gas flow rate, the input SiH4 concentration, and the reactor pressure. The advection of a small trimethylboron flow rate increases η and reduces the formation of powder, while the advection of a small disilane flow rate decreases η and favors the formation of powder. Unlike η, D is a location-dependent quantity. It is related to the SiH4 concentration in the plasma cpr, and to the phase of the growing Si film, whether the substrate is glass or a c-Si wafer. In order to investigate transient effects due to the RF matching, the precoating of reactor walls, or the introduction of a purifier in the gas line, we measure the gas residence time and acquire time-resolved SiH4 density measurements throughout the ignition and the termination of a plasma. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4921696]

I. INTRODUCTION

Silane (SiH4) is a process gas that is widespread throughout the semiconductor industry, especially in the production of solar modules and thin-film displays. The active silicon layers of such devices are typically deposited in plasma-enhanced chemical vapor deposition (PECVD) systems. While the input SiH4 flow rate is actively controlled, SiH4 is hardly ever monitored in the reactor itself or in the pumping line of PECVD systems. The purpose of this study is to show the relevance of monitoring physical quantities such as the SiH4 consumption efficiency, the SiH4 concentration in the plasma itself, or the time evolution of the SiH4 density after ignition, to name a few. Another aim of this work is to clarify the difference between two distinct physical quantities: the SiH4 consumption efficiency—as measured in the pumping line—and the SiH4 depletion fraction—as measured in the reactor itself. While some measurements presented here—although not all—may have been performed equally well with versatile instruments such as a residual gas analyzer (mass spectrometer),1–3 or a Fourier transform infrared spectrometer,4–7 we have opted for a tunable diode infrared laser spectrometer (TDL),8–10 in order to meet our stringent industrial requirement for a sensitive and non intrusive diagnostic tool that features a good time resolution. By splitting the laser beam, SiH4 could be monitored simultaneously in the reactor itself, in the surrounding chamber, and in the pumping line of a PECVD system over a wide range of process conditions.

II. EXPERIMENTAL SETUP

All Si films were deposited in a large-area, capacitively coupled, parallel-plate PECVD reactor. The reactor is a modified version of an industrial KAI-M PlasmaBox11,12 the interelectrode gap of which was reduced to 12.5 mm. Hydrogen and silane were introduced into the reactor through a 60 × 49 cm² radio-frequency-powered showerhead and were laterally pumped from one side. The longer electrode side (60 cm) was along the pumping direction, which we set as the x-direction in Fig. 1. The y-direction is set along the shorter electrode side (49 cm). A butterfly valve, installed between the pumping line and the reactor outlet, actively regulated the pressure in the reactor. Unless stated otherwise, the radio frequency (RF) and the deposition temperature were 40.68 MHz and 180°C, respectively.

A commercial RF probe (Z’scan, Advanced Energy Industries, Inc.) monitored the RF power at the exit of the matching network. Another probe measured the voltage on the RF-driven electrode itself. The effective power dissipated in the plasma was determined by subtracting the matching network losses from the power delivered by the RF generator, according to a method described by Horwitz.12 This
subtractive method is found to be in good agreement with other power measurements.13

As mentioned above, SiH4 was monitored in the PECVD system with a homebuilt TDLs.8 The infrared laser consisted of a commercial Peltier TDLs, a feedback quantum-cascade laser (QCL), which was tunable between 2241 and 2245 cm⁻¹. This wavenumber range is well suited to probe the R(9) multiplet of the ν3 vibrational band of SiH4.8 The collimated infrared beam of the TDLs was first modulated with a mechanical chopper at a frequency of 1 kHz, then was split into two beamlets. The mid-infrared beamlets were detected by commercial thermoelectric-cooled Hg-Cd-Te photovoltaic detectors. The preamplified detector signals were read by a computer-controlled lock-in amplifier, the reference signal of which was given by the chopper controller. In order to acquire a spectrum, the QCL was tuned by varying the supplied current.

One beamlet was guided through the pumping line, while the other was aligned toward the reactor in the y-direction at a distance of 7 mm from the RF-powered electrode. As pictured in Fig. 1, a custom-made lateral viewport was installed in the reactor wall in such a manner that the first reflection could exit the chamber again and be focused onto a detector (D2). In this manner, the SiH4 absorbance could be monitored simultaneously in the reactor, in the surrounding chamber, and in the pumping line. In a PECVD system that is differentially pumped such as ours—often referred to as a PlasmaBox—the pressure in the chamber is in principle much lower than the pressure in the reactor (during deposition). Therefore, we neglected in most cases the contribution of the chamber absorbance, which is measured by detector D2, to the total absorbance in the chamber and the reactor, measured by detector D1. If necessary, the absorbance in the reactor volume alone A_reac can be derived from

$$A_{\text{reac}} = A_1 - A_2 \frac{L_1 + L_2}{2L_2}, \quad (1)$$

where L₁ = 154 mm and L₂ = 119 mm are the distances pictured in Fig. 1, and where A₁ and A₂ are the absorbances measured by detector D1 and D2, respectively. Steady state measurements were acquired after stabilization of the plasma, while time-resolved measurements were acquired with a time resolution of 40 ms, which is sufficient considering the time required to deposit a monolayer of Si.

A homebuilt light scattering (LLS) device, installed at the reactor exhaust, monitored the formation of powder during all depositions. The excitation source of the LLS device was a frequency-doubled Nd:YAG laser emitting at 532 nm. Powder refers here to large (>50 nm) negatively charged particles that are trapped in the plasma and expelled from the reactor. They are produced in the last stage of a growth mechanism detailed elsewhere.14–18

The thickness and the crystallinity of films deposited on glass substrates were determined by profilometry and micro-Raman spectroscopy, respectively. The Raman crystallinity was measured with a commercial Renishaw Raman microscope in the back-scattering configuration according to a procedure described by Droz et al.19 The excitation source was an Ar⁺ laser emitting at 514 nm.

Preliminary tests, pictured in Fig. 2, were conducted in the reactor and in the pumping line without igniting a plasma. Since no gas was dissociated, the SiH4 and H2 flow rates in the pumping line were given by the input SiH4 flow rate Q_{SiH4} and the input H2 flow rate Q_{H2}, respectively. The total input flow rate, the input SiH4 concentration, and the pressure in the reactor were \( Q_{\text{tot}} = Q_{\text{SiH4}} + Q_{\text{H2}}, \) \( c = \frac{Q_{\text{SiH4}}}{Q_{\text{tot}}}, \) and \( p, \) respectively. Throughout this work, a flow rate always refers to a standard volumetric flow rate. This is essentially a mass flow rate that has been referenced to a certain gas composition and to an arbitrary pressure and temperature condition according to

$$Q = \frac{R \cdot T_o \cdot m}{M \cdot p_o}, \quad (2)$$

where \( Q \) is the standard volumetric flow rate of the gas, \( m \) is the mass flow rate of the gas, \( M \) is the molar mass of the gas, \( R \) is the ideal gas constant, \( p_o = 1 \text{ atm} \) is the standard pressure, and \( T_o = 0^\circ \text{C} \) is the standard temperature.

As expected from Beer’s law, the absorbance in the reactor increases linearly with the SiH4 partial pressure (or the SiH4 density) in the reactor. The SiH4 partial pressure is proportional to the input SiH4 concentration and to the total pressure, but is not affected by the total input flow rate. The situation in the pumping line is rather particular. By Beer’s law, the absorbance in the pumping line is proportional to the SiH4 density in the pumping line. In addition, Fig. 2 shows that the absorbance in the pumping line is proportional to the SiH4 flow rate, which is—by definition—proportional to the product of the SiH4 density and the SiH4 velocity. Consequently, the velocity of the SiH4 molecules in the pumping line is constant and independent of the reactor pressure, the SiH4 flow rate, or the H2 flow rate. This fortunate situation is due to the fact that the PECVD system is pumped by an overdimensioned vacuum system comprised of a roots and a rotary pump. It is not excluded that, in an

FIG. 1. Experimental arrangement of the TDLs and the PECVD system. Silane is monitored in the reactor volume (D1), in the chamber volume (D2), and in the pumping line (D3) of the PECVD system. Details of the TDLs are published elsewhere.8
other system, the absorbance in the pumping line would not be proportional to the SiH₄ flow rate.

III. FLUID MODEL

High-pressure, radio-frequency SiH₄/H₂ discharges were simulated with a self-consistent, two-dimensional, time-dependent fluid model. The latter combines several modules including the continuity equation, momentum and energy balances, heat transfer equations, and Poisson’s equation. The outcome is the density distribution of all chemical species and their flux towards surfaces, the temperature, and the electric field. The current version of the model considers 32 chemical species, which are subject to a total number of 235 chemical reactions including 169 gas-phase reactions and 66 plasma-surface interactions. The gas-phase reactions comprise electron impact dissociation, electron impact ionization, radical-neutral reactions, radical-radical reactions, ion-neutral reactions, ion-ion reactions, vibrational excitation and relaxation of SiH₄ and H₂, reactions of vibrational excited species with radicals, and the nucleation of small nanometer-sized particles (leading to the formation of dust). A non-exhaustive list of these reactions has been compiled by Kushner and Perrin. The rate constants of electron impact collisions and vibrational excitation of SiH₄ were derived from cross sectional data, whereas the rate constants of other reactions were either calculated or measured experimentally. Plasma-surface interactions involving ions, radicals, or atoms are described with sticking coefficients. Furthermore, we assumed that stable molecules (H₂, SiH₄, polysilanes) do not interact with the surface given our low substrate temperatures. Simulations required a computational effort of about 24 h on a regular personal computer. The purpose of the simulation work is not to fit experimental data neither to fine-tune the model briefly described here, but merely to give some physical insight.

IV. RESULTS AND DISCUSSION

A. The consumption efficiency versus the depletion fraction

Previously confused in the literature, and by the present authors themselves, the SiH₄ consumption efficiency and the SiH₄ depletion fraction actually represent two distinct physical quantities. If Q_pump is the standard flow rate of SiH₄ in the pumping line before ignition of the plasma and Q_pump is the standard flow rate of SiH₄ in the pumping line after ignition of the plasma, the SiH₄ consumption efficiency η is given by

\[ η = \frac{Q_pump - Q_{pump}^{off}}{Q_pump^{on}} = \frac{A_{pump}^{off} - A_{pump}^{on}}{A_{pump}^{off}} \]

where A_{pump}^{off} and A_{pump}^{on} are the SiH₄ absorbances in the pumping line before and after ignition of the plasma, respectively. In other words, if η = 50%, half of the silane molecules entering the PECVD reactor are expelled from the reactor in the form of silane, while the other half may contribute to the film growth, or react to form powder or polysilane molecules, as sketched in Fig. 3. In the literature, η is also referred to as the SiH₄ utilization efficiency, or as the SiH₄ dissociation efficiency. We prefer to avoid this latter terminology, as SiH₄ may be consumed through other channels than electron impact dissociation. Moreover, η must not be confused with the SiH₄ dissociation rate k_{ne} expressed in s⁻¹ and defined as the number of SiH₄ molecules dissociated by electron impact per unit time per unit volume per unit SiH₄ density. We would also like to point out that the right-hand side of Eq. (3) only holds true if the SiH₄ absorbance in the pumping line is proportional to the SiH₄ flow rate, as discussed under Sec. II.

Unlike η, the SiH₄ depletion fraction is a position-dependent physical quantity, which expresses the fraction by which the silane density decreases in the reactor upon
ignition of a discharge. In particular, it varies along the inter-electrode distance. Under uniform deposition conditions, it is however not expected to vary along the pumping direction (x-direction in Fig. 1). The value measured in this work is an integrated value over the laser beam, which had a diameter of ~2 mm and which was aligned perpendicular to the pumping direction at a distance of 7 mm from the RF-powered electrode. If \( n_{\text{off}} \) and \( n_{\text{on}} \) are the SiH\(_4\) densities in the ground state inside the reactor before and after ignition of the plasma, the SiH\(_4\) depletion fraction \( D \) can be expressed as

\[
D = \frac{n_{\text{off}} - n_{\text{on}}}{n_{\text{off}}} = \frac{A_{\text{off}} - A_{\text{on}}}{A_{\text{off}}},
\]

where \( A_{\text{off}} \) and \( A_{\text{on}} \) are the absorbances in the reactor measured at a given wavenumber before and after ignition of the plasma, respectively. In other words, if \( D = 50\% \) at a given position within the reactor, the density of SiH\(_4\) molecules in the ground state decreases by 50\% at that position upon ignition of the plasma. As a reminder, the infrared laser probes transitions from the ground state to the \( \nu_3 \) vibrational band of silane. Therefore, if higher vibrational states are excited upon ignition of the plasma, the absorbance will decrease as a result of the ground state depopulation in addition to, e.g., electron impact dissociation. Whereas the SiH\(_4\) molecules are fully relaxed in the pumping line, we cannot exclude a contribution of vibrationally excited species in the reactor. Although we have neglected the discussion of such species in this work, the SiH\(_4\) density in the reactor always refers here to the SiH\(_4\) density of molecules in the ground state, rather than the total density of SiH\(_4\) species inside the reactor (as one would expect in, e.g., mass spectroscopic studies). Furthermore, we would like to point out that the right-hand side of Eq. (4) only holds true if the kinetic gas temperature does not increase significantly upon ignition of the plasma, which is roughly the case under our effective RF power densities of \( \leq 0.4 \text{ W/cm}^2 \). In general, an integration of the broadened absorption line profile would be required to yield the SiH\(_4\) density in the ground energy level.

In Fig. 4, we propose to verify some trends predicted by a simple zero-dimensional plasma chemistry model derived by Strahm et al. that assumes only one type of silane radical. The model can be solved analytically and yields an expression of \( \eta \) that depends only on the SiH\(_4\) dissociation rate \( k_n \) and the gas residence time \( \tau \). Furthermore, if we assume that \( kn_e \propto P_{\text{eff}} \) and that \( \tau \propto \frac{1}{Q_{\text{tot}}} \) (as discussed under Sec. IV E), we obtain
where \( a \) is the only fitting parameter in Fig. 4.

In order to test the plasma chemistry model above, we measured \( \eta \) as a function of the effective RF power density dissipated in the plasma \( P_{\text{eff}} \), the total input flow rate \( Q_{\text{tot}} = Q_{\text{SiH}_4} + Q_{\text{He}} \), the input \( \text{SiH}_4 \) concentration \( c = \frac{Q_{\text{SiH}_4}}{Q_{\text{tot}}} \), and the pressure in the reactor \( p \). The four measurement series are depicted in Fig. 4. While performing such series, it is important to vary one process parameter at a time, while maintaining all others constant. A radio frequency of 40.68 MHz was also kept constant throughout this work. Sansonnenus et al. have shown that \( C \) increases as the radio frequency is tuned from 10 to 70 MHz at a constant RF power.\(^5\) The constant effective RF power condition is experimentally difficult to fulfill, as it can only be measured after ignition of the plasma. During preliminary tests, we determined the RF power density \( P_{\text{gen}} \) that the generator had to deliver in order to maintain \( P_{\text{eff}} \) constant. In Fig. 4, we also picture the RF power coupling efficiency \( \eta_{\text{RF}} \), defined as

\[
\eta_{\text{RF}} = \frac{P_{\text{eff}}}{P_{\text{gen}}},
\]

As discussed in further detail by Spiliopoulos et al.\(^28\) or Böhm et al.,\(^29\) \( \eta_{\text{RF}} \) varies considerably with the RF power (Fig. 4(a)) and the pressure (Fig. 4(d)). It is important to realize that matching network losses may be as high as 40\% at low power (Fig. 4(a)) or at low pressure (Fig. 4(d)), and that measurement series may be misinterpreted if such effects are not taken into account. In this work, we took care to avoid such artifacts by performing measurement series at a constant \( P_{\text{eff}} \) whenever required.

The model derived by Strahm et al. also predicts that

\[
\eta = \frac{k_{\text{ne}} \cdot \tau}{k_{\text{ne}} \cdot \tau + 1} = \frac{a \cdot P_{\text{eff}}}{a \cdot P_{\text{eff}} + \frac{P}{Q_{\text{tot}} + 1}},
\]

where \( a \) is the only fitting parameter in Fig. 4. To illustrate the limitations of this analytical zero-dimensional model, we have applied the numerical two-dimensional model, briefly described under Sec. III, in order to simulate the pressure series presented in Fig. 4(d). Whereas \( \text{SiH}_4 \) is solely consumed through electron impact dissociation in the analytical model (reaction \( R_1 \) below), the 7 most significant \( \text{SiH}_4 \) reaction paths in the numerical model are

\[
\begin{align*}
\text{e}^- + \text{SiH}_4 &\rightarrow \text{SiH}_3 + (4-n)\text{H}, \quad n = 0-3, \quad (R1) \\
\text{e}^- + \text{SiH}_4 &\rightarrow \text{SiH}_4^- + (4-n)\text{H}, \quad n = 2-3, \quad (R2) \\
\text{H} + \text{SiH}_4 &\rightarrow \text{SiH}_3 + \text{H}_2, \quad (R3) \\
\text{SiH}_2 + \text{SiH}_4 &\rightarrow \text{Si}_2\text{H}_6, \quad (R4) \\
\text{H}_2^+ + \text{SiH}_4 &\rightarrow \text{SiH}_3^+ + 2\text{H}_2, \quad (R5) \\
\text{SiH}_4^- + \text{SiH}_4 &\rightarrow \text{Si}_2\text{H}_5^- + \text{H}_2, \quad (R6) \\
\text{SiH}_2 + \text{H}_2 &\rightarrow \text{SiH}_4. \quad (R7)
\end{align*}
\]

At a low pressure of 1 mbar, the most significant \( \text{SiH}_4 \) reaction path is indeed electron impact dissociation (\( R_1 \)), as illustrated under Fig. 6(a). At higher pressures, the reaction rates of \( R_1 \) and \( R_2 \) drop, as the electron temperature and density decrease, which both affect the population of high-energy electrons. \( \text{H} \) abstraction (\( R_3 \)) becomes then the most significant consumption path of \( \text{SiH}_4 \). It reaches a maximum around 4 mbars when the concentration of \( \text{H} \) atoms is maximized. Furthermore, when the pressure increases further up to 12 mbars, two trends compete against each other. On the one hand, secondary gas-phase reactions become more significant (\( R_4 \)),\(^22\) which consumes \( \text{SiH}_4 \) even further. On the other hand, the regeneration of \( \text{SiH}_4 \) increases as well (\( R_5 \)),\(^22\) thus reducing the net reaction rate computed in Fig. 6(b). The computed net reaction rate has the same behaviour as the measured pressure series trend illustrated in Fig. 4(d). In the latter, the residence time, which increases with...
pressure, softens the sharp decrease observed at high pressure in Fig. 6(b).

B. The film growth rate and the polysilane/powder formation rate

In the absence of polysilane and powder formation, any amount of SiH₄ consumed contributes to film growth. Assuming a uniform deposition over the electrode area, one can thus estimate a film growth rate $R_d$ from the input SiH₄ flow rate $Q_{SiH₄}$, the SiH₄ consumption efficiency $\eta$, and the inner surface of the reactor $A_{\text{reac}}$. If $R_d$ is expressed in A/s, $Q_{SiH₄}$ is expressed in sccm (standard cubic centimeters per minute at 1 atm and 0°C), and $A_{\text{reac}}$ is expressed in cm², we have

$$R_d = \alpha \cdot \frac{\eta \cdot Q_{SiH₄}}{A_{\text{reac}} \cdot \rho_{Si}}.$$

(7)

where $\alpha = 2088 \frac{g}{cm \cdot sccm \cdot s}$ is system-independent, and $\rho_{Si}$ is the silicon mass density of the film expressed in g/cm³. Given the atomic percentage of hydrogen in such films, $\rho_{Si}$ can be approximated by the mass density of the film itself, which is 2.2–2.3 g/cm³ for a-Si:H and µc-Si:H films.31,32

In Fig. 7, the actual film growth rate $R_d$, measured by profilometry, is compared to the film growth rate $R_d^c$ that one would expect had the film incorporated all the SiH₄ that was consumed. In powder-free conditions, $R_d^c$ and $R_d$ are in good agreement with each other, whereas $R_d^c$ is always overestimated in powder-rich regimes, as expected. This correlation is also illustrated in Fig. 8, where the RF power delivered by the generator was tuned from a powder-free regime ($P_{\text{gen}} = 0.1 W/cm²$) to a powder-rich regime ($P_{\text{gen}} > 0.1 W/cm²$).

In the absence of polysilane/powder formation, many deposition rate series reported in the literature can be explained in light of Eq. (7) and Fig. 4. As the formation of powder increases above a threshold value, a significant amount of SiH₄ is lost and $R_d$ becomes lower than $R_d^c$. The difference $R_d^c - R_d$ measures the total amount of SiH₄ lost in polysilane and powder, whereas a LLS device detects the presence of powder only. For a given series, we have previously shown that $R_d^c - R_d$ scales well with the LLS signal, as measured at the reactor exhaust. It is, however, not

FIG. 6. In (a), we display the reaction rates of reactions that consume SiH₄ ($R_1$–$R_6$) and that generate SiH₄ ($R_7$) according to a fluid model described in Sec. III. In (b), we compute the total reaction rate $\sum_{i=1}^{6} R_i - R_7$. The process parameters were the same as in Fig. 4(d).

FIG. 7. Expected film growth rate $R_d^c$ assuming that all the SiH₄ that is consumed is incorporated into the film (in situ measurement) versus actual film growth rate $R_d$ measured by profilometry (ex situ measurement). Plasma regimes featuring a LLS signal above a given threshold value (20 mV) are depicted in red.

FIG. 8. Powder formation rate as a limiting factor to the achievable deposition rate. The power density delivered by the RF-generator is increased from a powder-free plasma regime (LLS signal < 20 mV) to a powder-rich plasma regime (LLS signal > 20 mV). The data were measured at $Q_{SiH₄} = 100 sccm$, $Q_{H₂} = 800 sccm$, and $p = 4$ mbar.
excluded that some regimes could feature a significant amount of polysilane formation that does not lead to much powder formation. The threshold LLS signal value above which the production of powder becomes significant is not an absolute value, but needs to be calibrated for each deposition system.

At first glance, Eq. (7) suggests that one may deliberately increase the deposition rate by increasing $Q_{\text{SiH}_4}$. One must, however, bear in mind that $\eta$ decreases as $Q_{\text{tot}}$ increases, as explained under Sec. IV A. This effect may be counteracted by increasing the RF power density (Fig. 4(a)) and—up to a certain point—by increasing the pressure in the reactor (Fig. 4(d)). Ultimately, the maximum achievable deposition rate is limited by the formation of powder, where any additional amount of silane that is consumed translates into powder formation rather than into a faster growing film. This limitation is well illustrated in Fig. 8, where the amount lost in polysilane and powder accounts for 47% of $R_d$ at $P_{\text{eff}} = 0.44$ W/cm$^2$. On the one hand, powder is thus a major limiting factor to the maximum achievable deposition rate—even at our reduced interelectrode gap of 12.5 mm—and a potential source of inhomogeneous and instable plasma conditions. On the other hand, powder can be seen as a by-product of secondary gas-phase reactions, which have been found to be favorable process conditions to deposit device-grade $\mu$-c-Si:H at a high rate. Moreover, the presence of powder did not seem to be detrimental during the deposition of a-Si:H films for the surface passivation of c-Si wafers.

### C. The catalytic effect of trimethylboron (TMB) and $\text{Si}_2\text{H}_6$

The deposition rate of p-doped layers is slightly increased with respect to intrinsic layers deposited under the same conditions. We investigated the origin of this effect under different plasma regimes. In Fig. 9, we show that the adjunction of a small TMB flow rate increases $\eta$ and decreases the formation of powder, which both contribute to a higher deposition rate. A similar effect is expected if diborane is added instead of TMB.34 Surface reactions models, proposed by Perrin et al. and Sato et al.,35,36 describe this catalytic effect, but it remains unclear whether they could also account for the powder formation inhibition reported here. Another catalytic effect is presumably observed upon the adjunction of disilane ($\text{Si}_2\text{H}_6$). Early studies have indeed reported that $\text{Si}_2\text{H}_6$ or higher order polysilane molecules, could serve as additives in order to increase the growth rate of $\mu$-c-Si:H films,37 which currently is a bottleneck in the fabrication of Micromorph solar cells. Supposedly, the increase in growth rate is due to chemical or electron energy effects, rather than electrical artifacts (such as a variation of $\eta_{\text{EF}}$).38 We have investigated the effect of disilane under various plasma regimes, but we could not confirm such reports. In fact, we have always evidenced the contrary behavior, illustrated in Fig. 10, namely, an increase in powder formation and a decrease of $\eta$, which both contribute to a lower deposition rate (see also Sec. IV B). The effect on the film crystallinity has not been investigated in this work.

**FIG. 9.** Powder formation inhibition and silane consumption increase upon the adjunction of a small TMB flow rate, as studied in a powder-rich plasma regime (a) and a nearly powder-free plasma regime (b). The input TMB concentration is understood here as the ratio of the input TMB flow rate $Q_{\text{TMB}}$ to the total input flow rate $Q_{\text{tot}}$ (where $Q_{\text{tot}} = Q_{\text{SiH}_4} + Q_{\text{H}_2} + Q_{\text{TMB}}$). Both regimes were measured at $Q_{\text{tot}} = 100$ sccm, $Q_{\text{H}_2} = 900$ sccm, and $p = 4$ mbar. The power density delivered by the RF-generator $P_{\text{RF}}$ was 0.31 W/cm$^2$ and 0.10 W/cm$^2$ in regimes (a) and (b), respectively.

### D. Thin-film silicon phase transitions

If we define a silane concentration in the plasma $c_p$ as the ratio of the silane density in the reactor to the total density, and if $p$ is kept constant, $c_p$ can be expressed as a function of $D$ according to $c_p = (1 - D)c$, where $c$ is the input silane concentration as defined earlier. A relevant parameter that determines the phase of growing Si film is the flux ratio between hydrogen atoms and silane radicals impinging on the film surface.38 Strahm et al. have correlated this flux ratio to $c_{\text{ps}}$, and have shown that, for a given deposition temperature, $\mu$-c-Si:H and a-Si:H systematically grow on glass below and above a threshold $c_p$ value, respectively.6 Device-grade $\mu$-c-Si:H may therefore even be obtained from a pure silane flow ($c = 1$), provided the plasma is sufficiently depleted ($D \geq 97.2\%$).40 In good agreement with these previous studies, we report in Fig. 11 an a-Si:H to $\mu$-c-Si:H transition region for $1 \leq c_p \leq 2.8\%$, regardless of other input parameters such as the input $\text{SiH}_4$ flow rate, the input $\text{H}_2$ flow rate, the RF power, or the pressure in the reactor. The depositions in Fig. 11 were performed on glass substrates that were precoated with p-doped $\mu$-c-Si:H. For films deposited on bare glass substrates, the Raman crystallinity—as expected—decreases for a given set of deposition parameters within the transition region, but the transition region itself is not shifted with respect to $c_{\text{ps}}$.41 A similar behavior is observed for thin films deposited on mirror-polished (100) c-Si wafers following native oxide
FIG. 10. Powder formation increase and silane consumption decrease upon the adjunction of a small disilane (Si2H6) flow rate, as studied in a powder-rich, high-depletion plasma regime (a) and a powder-free, low-depletion plasma regime (b). The input Si2H6 concentration is understood here as the ratio of the input Si2H6 flow rate, 800 sccm, to the total input flow rate (where 5.5 mbars, 910 sccm, 0.32 W/cm2. The data presented in (a) were measured at QH2 = 2500 sccm, QSiH4 = 2550 sccm, p = 1 mbar, and Pgen = 0.12 W/cm2.

FIG. 11. Silane concentration in the plasma c_p = (1 - D)c as a determining factor for the a-Si:H to μc-Si:H transition. The transition region is situated between 1% and 2.8% for thin films deposited at 453 K on a non-crystalline substrate (glass, a-Si:H, or μc-Si:H). Similarly, thin films deposited on a mirror-polished (100) c-Si substrate yield an epitaxy to a-Si:H transition region situated between 3% and 9%.41

E. SiH4 residence and stabilization times

For certain applications, such as the fabrication of Si heterojunction solar cells,44 extremely well-controlled short depositions are required. In such a case, transient effects may have a significant impact on the deposited films, which are only a few nanometers thin. In order to investigate such transient effects, the laser wavelength was adjusted to match the top of a SiH4 absorption line. The SiH4 density in the reactor was then acquired with a time resolution of 40 ms at a distance of 7 mm from the RF-powered electrode. The laser wavelength was stable over the total acquisition time. This rudimental technique was applied for the sake of convenience and was sufficient to discuss the SiH4 transients presented below. For a continuous control of SiH4 over the duration of a whole deposition process, advanced techniques such as wavelength modulation would be required.

Without igniting a plasma, we recorded the time evolution of the SiH4 density n(t) after engaging a SiH4 flow at an instant t = t0 and derived the gas residence time τ in the reactor of the PECVD system. Throughout the measurement, the H2 flow and the pressure in the reactor p were kept constant. From simple fluid dynamic considerations, one can show that n(t) and τ are given by

\[ n(t) = n^\infty + (n^0 - n^\infty) \cdot e^{-(t-t_0)/\tau}, \quad (8) \]

\[ \tau = \frac{T_{p} V}{T_{p_{0}} Q_{tot}}, \quad (9) \]

where t ≥ t0, n^\infty = n(t → ∞), n^0 = n(t0), V is the total reactor volume, and T is the gas temperature. Similar considerations apply to the reverse situation, where H2 and SiH4 flows are maintained across the reactor and where the SiH4 flow is stopped at an instant t = t0 while keeping the pressure in the reactor constant. The experimental procedure consisting of stopping the SiH4 flow is actually preferred, because it avoids artifacts due to the dead volume comprised between the mass flow controller (MFC) and the subsequent valve. Another artifact is introduced if a gas purifier is installed after the MFC, as pictured in Fig. 12. The purifier, whose primary role is to decrease the oxygen and moisture content of the carrier gas, presents a path of high resistance to the gas flow, which in turn is responsible for a long stabilization time. In the presence of such artifacts, the SiH4 density rise time (or the SiH4 density decay time) is a measure of this gas stabilization time rather than of the gas residence time τ. Long stabilization times can have severe consequences in processes during which gas flow ratios are changed.
To correctly reproduce the situation described by Eq. (9), the SiH4 flow must be engaged (or stopped) instantaneously, i.e., the reaction times of the MFC and the butterfly valve must be much shorter than \( \tau \) itself. The SiH4 density rise time (or the SiH4 density decay time) is then a true measurement of \( \tau \). In order to exclude the presence of artifacts, we have measured \( \tau \) as a function of the reactor pressure and the total flow, as illustrated in Fig. 13. The experimental data could be well fitted with the linear relation derived under Eq. (9).

In addition to the time-resolved SiH4 density in the reactor, our experimental arrangement, described under Sec. II, enabled us to acquire the time-resolved SiH4 density in the chamber of the PECVD system. As pictured in Fig. 12, we could also derive a gas residence time for the chamber volume on the basis of Eqs. (8) and (9), where \( p \) and \( Q_{\text{tot}} \) should be understood here as the reactor pressure and the gas leakage from the reactor into the chamber. For a given set of parameters, the residence time in the chamber is much longer than the residence time in the reactor, because the reduced pressure in the chamber outweighs the gas leakage from the reactor into the chamber (\( \tau \propto \frac{p}{Q_{\text{tot}}} \)).

**F. Plasma ignition and termination**

The time-resolved SiH4 density was recorded throughout the ignition of various plasmas until steady state conditions were reached. The plasma was solely ignited by action of the RF generator and the automated capacitively coupled matching box, the initial capacitance values of which could be adjusted. Matched initial capacitance values were determined during a preliminary set of experiments. In Fig. 14, typical acquisitions are displayed. The initial SiH4 density overshoot in Fig. 14(a) is due to the unmatched capacitance values, while the initial overdepleted silane in Figs. 14(a) and 14(b) is due to the absence of a precoating of the reactor walls. The latter finding demonstrates that the inner surface of the reactor has an influence on the bulk plasma properties. We expect this effect to be less pronounced in a reactor with a larger interelectrode gap and, therefore, a smaller surface to volume ratio. When the initial capacitance values are matched and the reactor walls are precoated with silicon, steady state conditions may be reached within 0.4 s following the ignition of a plasma—as illustrated under Fig. 14(d)—which is in good agreement with previous studies conducted on a similar reactor design.45 Open-electrode laboratory-scale reactors typically feature much longer transition times of up to several dozens of seconds due to silane back-diffusion from the surrounding chamber volume.7,40,46,47 Such issues are critical, because the material properties of an interface layer, deposited during the initial transient state, may significantly differ from those of the bulk, deposited under steady state conditions.7,46

The time-resolved SiH4 density was also acquired throughout the termination of a plasma, as illustrated under Fig. 15 for two sets of process conditions (A and B). The plasma was simply terminated by switching off the RF-power. According to the linear relation derived under Fig. 13, the gas residence time of processes A and B was 442 ms and 1.87 s, respectively. The latter is similar to the respective transition times required to reach steady state conditions upon termination of the plasma.
V. CONCLUSIONS

The SiH\textsubscript{4} consumption efficiency $\eta$ and the depletion fraction $D$ can be measured by monitoring silane in the pumping line and the reactor of a PECVD system, respectively. Although they are closely related to one another, $\eta$ and $D$ represent two distinct physical quantities. While $\eta$ is the SiH\textsubscript{4} consumption efficiency of the overall PECVD system, $D$ is position-dependent and expresses the fraction by which the SiH\textsubscript{4} density decreases upon ignition of a discharge. Under uniform deposition conditions and in the absence of polysilane or powder formation, $\eta$ is proportional to the deposition rate. Above a certain powder formation threshold, any additional amount of SiH\textsubscript{4} consumed translates into increased powder formation rather than into a faster growing Si film. The phase of the growing Si film is correlated to the silane concentration in the plasma $c_p$, where $c_p = (1 - D)c$. On a non-crystalline substrate (glass, a-Si:H, µc-Si:H), microcrystalline Si and amorphous Si systematically grow below and above a threshold $c_p$ value, respectively. Within the transition region, situated between 1% and 2.8% for thin films deposited at 453 K, one cannot predict the phase of the growing Si film. Similarly, on a c-Si substrate, Si epitaxy and a-Si:H systematically grow below and above a threshold $c_p$ value, as found in a separate study.\textsuperscript{41}

The catalytic effect of TMB and disilane has been investigated in powder-free and powder-rich deposition regimes. The adjunction of a small TMB flow rate increases $\eta$ and reduces the formation of powder, which both contribute to a higher deposition rate. Contrary to earlier reports, the adjunction of a small Si\textsubscript{2}H\textsubscript{6} flow rate decreases $\eta$ and favors the formation of powder, which both contribute to a lower deposition rate.

Finally, in order to investigate transient effects due to the RF matching, the precoating of reactor walls, or the introduction of a purifier in the gas line, we measured the gas residence time and acquired time-resolved SiH\textsubscript{4} density measurements throughout the ignition and the termination of a plasma. When the initial capacitance values are matched and the reactor walls are precoated, steady state conditions may be reached within 0.4 s following the ignition of a plasma. The absence of a precoating of the reactor walls is responsible for an initial overdepleted silane, which

![FIG. 14. Plasma ignition in a clean PECVD reactor with unmatched initial capacitance values (a), in a clean reactor with matched initial capacitance values (b), and in a precoated reactor with matched initial capacitance values (c) and (d). In (a), (b), (c), and (d), the transition time to reach steady state conditions is 4.5 s, 3.7 s, 1.1 s, and 0.4 s, respectively.](image-url)

![FIG. 15. Plasma termination in a PECVD reactor for process A (a) and process B (b). In process A, $Q_{\text{Sil}}$, $Q_{\text{H2}}$, and $p$ were 45 sccm, 1980 sccm, and 4 mbars, respectively. In process B, a pressure of 1 mbar was maintained in the reactor with a pure input SiH\textsubscript{4} flow rate of 120 sccm. Upon termination of the plasma, the SiH\textsubscript{4} recovers its undepleted value with a time constant of 390 ms (a) and 1.82 s (b) (as obtained from an exponential fitting procedure). The time constant is similar to the gas residence time of the respective process.](image-url)
demonstrates that the inner surface of the reactor has an influence on the bulk plasma properties.

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